**Hydrology and
Earth System
Sciences**

HESS Opinions

"Biological catalysis of the hydrological cycle: life's thermodynamic function"

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Abstract. Darwinian theory depicts life as being overwhelmingly consumed by a fight for survival in a hostile environment. However, from a thermodynamic perspective, life is a dynamic, out of equilibrium process, stabilizing and coevolving in concert with its abiotic environment. The living components of the biosphere on the Earth's surface of greatest biomass, the plants and cyanobacteria, are involved in the transpiration of a vast amount of water. Transpiration is part of the global water cycle, and it is this cycle that distinguishes Earth from its apparently life-barren neighboring planets, Venus and Mars. The dissipation of sunlight into heat by organic molecules in the biosphere, and its coupling to the water cycle (as well as other abiotic processes), is by far the greatest entropy-producing process occurring on Earth. Life, from this perspective, can be viewed as performing an important thermodynamic function, acting as a dynamic catalyst by aiding irreversible abiotic processes such as the water cycle, hurricanes, and ocean and wind currents to produce entropy. The role of animals in this view is that of unwitting but dedicated servants of the plants and cyanobacteria, helping them to grow, and to spread into initially inhospitable areas.

1 Preamble

It is the premise of this article that, since its inception some 3.8 billion years ago, life has been intimately connected with the hydrological cycle. Through physical-chemical mechanisms, described below, life has conserved the amount of water on Earth, has kept Earth's temperature within the narrow range suitable for the three phases of water, and has augmented the amount of water in the water cycle. This biotic-abiotic coupling is argued to be a manifestation of established non-equilibrium thermodynamic principles, which indicate that irreversible processes couple to remove impediments to greater global entropy production.

Biology, dispersed throughout Earth's surface, has adjusted the gases of Earth's atmosphere in such a manner that the most intense part of the solar spectrum can penetrate the atmosphere and reach the surface to be intercepted by biology. The covalent bonding of atoms in organic pigments leads to collective electronic excitations compatible with these high photon energies. Inter-system crossing and vibrational relaxation to the ground state of these excited molecules when in water lead to rapid dissipation of the solar photons into heat, and this is the major source of entropy production on Earth. An important part of the energy of the dissipated photons is channeled into the hydrological cycle through the latent heat of vaporization of surface water. By dissipating the ensuing surface to atmosphere temperature gradient, the hydrological cycle further increases the entropy production of Earth. This thermodynamic view has implications to a more general theory of evolution and to the theory of Gaia (Lovelock, 1988; 2005).

The Introduction to this paper presents the non-equilibrium thermodynamic principles, in particular Onsager's principle, which explains the coupling of biology to the hydrological cycle. Section 3 calculates the global entropy production of the planets from knowledge of the incident and emitted photon spectra. Earth's entropy production per unit surface area is found to be significantly larger than

that of either Venus or Mars, tentatively suggesting the influence of life. Section 4 gives evidence for the proposition that the important thermodynamic work performed by life is neither photosynthesis nor metabolism, but rather evapotranspiration, which couples directly to the hydrological cycle. Section 5 describes this coupling, including the details of how organic pigments, water, and the water cycle all participate to dissipate the incident high energy photons from the Sun. Section 6 presents calculations demonstrating how cyanobacteria and other organic material at the ocean surface increase the photon dissipation and evaporation rate of the surface water, much in the same manner as land plants increase photon dissipation and evapotranspiration over land. Section 7 presents evidence for an increase in the coupling of life to the hydrological cycle over the evolutionary history of life on Earth. Section 8 discusses the supporting role of animals in this thermodynamic view. Finally, Sect. 9 summarizes the evidence for biology catalyzing the water cycle and concludes with tentative implications for a more general evolutionary theory and the theory of Gaia.

2   Introduction

About 4.57 billion years ago, the Earth condensed out of a nebula of gas and dust to be illuminated by a volatile Sun which finally settled down as a main sequence star about 50 million years after its birth (Zahnle et al., 2007). The Earth was born with a primitive atmosphere, oceans, and surface, but these were continually transformed during this initial period by an evolving Sun, heat outflow from the Earth, and by constant bombardment of asteroids, comets, and even large protoplanets (Zahnle et al., 2007). Then, approximately after the end of a cataclysmic era, recorded on the Moon as the "lunar late heavy bombardment" (ca. 3.8 Ga), possibly caused by gravitational effects of the migration of the outer planets (Zahnle et al., 2007), the physical conditions on Earth stabilized and life emerged.

The emergence of life on Earth has mostly been considered as an extraordinary event, and its evolution in complexity and global extent attributed to an inherent survival instinct programmed into the individual operating in a hostile environment. Darwin himself suggested that life was at the mercy of the forces of nature and would necessarily adapt by means of natural selection to the demands of the external environmental. However, it has since become apparent that life plays a pivotal role in shaping its physical environment (Lovelock, 1988). What once appeared to be biotic evolution in response to abiotic pressure is now seen as co-evolution of the biotic together with the abiotic to greater levels of complexity, perhaps stability, and, of most interest here, greater entropy production (Ulanowicz and Hannon, 1987).

Entropy production is the rate of the tendency of nature to explore the multitude of microstates that underlies the macroscopic world that we perceive. This results from the microscopic nature of material, the multitude of ways to distribute the conserved extensive thermodynamic variables (energy, momentum, angular momentum, etc.) over the myriad of microscopic degrees of freedom, and the rather special initial conditions at the creation of our universe (Penrose, 2004). Macroscopic states consistent with a larger number of microstates are simply more probable, and thus nature tends to move towards these macrostates of greater microstate multiplicity; the actual path taken is determined by the initial conditions, the allowed kinetics, external constraints, and external perturbations.

All irreversible processes, the hydrological cycle and living systems included, arise and persist to produce entropy. Entropy production is not coincidental to the process, but rather the reason for its very existence. A fundamental characteristic of nature is the search for routes to greater global entropy production, often building on pre-existing routes by coupling new irreversible processes to existing ones. Onsager (1931) has shown how diverse irreversible processes can couple in order to remove impediments to greater global entropy production (Morel and Fleck, 1989). In general, the more complex the dissipative structuring in space and time (i.e. involving many coupled irreversible processes with embedded hierarchal levels and interactions of long spatial and temporal extent), the greater is the overall entropy production in the systems interaction with its external environment (Onsager, 1931; Prigogine et al., 1972a,b; Lloyd and Pagels, 1988).

There is historical evidence that biota have evolved to ever more complex and interconnected systems of greater entropy production (Zotin, 1984, 1990). Examples are the cell, ecosystems, and human society. Darwinian theory suggest that this is a result of evolution through natural selection based on mutation, individual fitness, and a struggle for the raw materials of existence. However, only 27 yr after publication of the theory of evolution through natural selection, Boltzmann (1886) wrote: "*The general struggle for existence of animate beings is therefore not a struggle for raw materials nor for energy which exists in plenty in any body in the form of heat – but a struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth.*" A more assertive view suggests that it is the struggle to increase the global entropy production of Earth which drives evolution through natural selection at all hierarchal levels.

In this thermodynamic view, organisms are not individual entities endowed with a meta-physical "will to survive", but instead are coupled, irreversible flows (both biotic and abiotic) which arise in response to thermodynamic potentials, which define their environment. These local thermodynamic potentials are created by other irreversible processes dissipating thermodynamic potentials on a still higher level, and so on up until reaching the highest hierarchal level of the Earth in its solar environment.

The thermodynamic view has the advantage of avoiding the tautology in Darwinian theory and of explaining co-evolution of the biotic with the abiotic by appealing to established thermodynamic law. It also accommodates selection on all levels; those couplings, or hierarchies of couplings, which lead to greater global entropy production of the Earth in its solar environment, will be most probable. The Darwinian view sees evolution as a bottom-up process, in which the individual, through its "will to survive", takes precedent, whereas the thermodynamic view sees evolution as a top-down process, in which the global entropy production of Earth in its solar environment, through its "tendency to increase", takes precedent.

Such a thermodynamic view provides new insight into the dynamics of Earth system processes that otherwise may not have been recognized. For example, it is the hypothesis of this paper that life is an example of an irreversible biotic process that arose and evolved by coupling to an abiotic irreversible process, the hydrological cycle. Such co-evolution of the biotic with the abiotic, difficult to reconcile within traditional Darwinian theory, fits perfectly well within the framework of non-equilibrium thermodynamics in which dissipative systems spontaneously arise, couple, and co-evolve in such a manner so as to increase the global entropy production of the Earth in its interaction with its solar environment (Onsager, 1931; Prigogine, 1972a,b; Ulanowicz and Hannon, 1987; Swenson, 1989; Kleidon and Lorenz, 2005; Michaelian, 2005, 2009).

The relevance of entropy production to the origin of life has been considered elsewhere (Michaelian, 2009, 2011). The present paper studies how life has co-evolved with the water cycle to create an ever more complex ecosphere (defined as the greater entity composing the biosphere, lithosphere, atmosphere, and hydrosphere, including all physical processes occurring therein), driven by the increase in entropy production afforded to the Earth in its solar environment.

3 Global entropy production of the planets through photon dissipation

Planets approximate closed thermodynamic systems, kept out of equilibrium by the hot photon source of the Sun and the cold photon sink of outer space. In the case of Earth, the absorption and dissipation of high energy photons into low energy photons is facilitated, in large part, by the organic pigments in plants and cyanobacteria in the presence of water. Life, in fact, is fundamental to the water cycle on many levels, and this will be analyzed in Sect. 4 through Sect. 8. In this section, we obtain an indication of the relevance of life and water to Earth's global entropy production by comparing the entropy production of Earth with that of its apparently lifeless and waterless neighboring planets, Venus and Mars.

The relative thermodynamic simplicity of the sun-planet-space system, with little coupling to other irreversible processes occurring in the solar system or universe, permits a reliable calculation of the planet's entropy production. This was first attempted by Aoki (1983) using a heat flow equation for the entropy production: $dS/dt = Q_{rad}/T_{rad} - Q_{in}/T_{in}$, where Q_{rad} and Q_{in} are radiated and incident heat fluxes at black-body temperatures T_{rad} and T_{in}, respectively. Although leading to reasonably accurate predictions for Earth, this type of analysis suffers from a number of deficiencies related to the distinct nature of photons from heat. Heat flow analysis neglects the wavelength-dependent increase in entropy that the photon flux experiences due to its expansion in space on leaving the Sun (Wu et al., 2011). Radiation pressure is also ignored. Furthermore, a portion of the photons, corresponding to the planet's wavelength-dependent albedo, is reflected directly back into space with no change in wavelength. This scattering from the atmosphere or surface leads to a more isotropic distribution of photons than that of the incident beam, and thus also contributes to a wavelength-dependent entropy production not included in heat flow calculations. The net entropy flux of Earth calculated through heat flow equations is, in fact, about 30 % to 40 % lower than that obtained through an accurate photon analysis (Wu and Liu, 2010). Finally, heat flow calculations necessarily presume equilibrium black-body spectra, at a particular temperature, for the incident and emitted radiations, while photon calculations use the actual empirically determined incident and emitted non-equilibrium spectra, if available.

In this section, a full photon calculation of a planet's entropy production is performed following Wu and Liu (2010), including the corrections for the expanding incident photon flux considered in Wu et al. (2011). Although gray-body approximations will be used for the incident and emitted spectra (for lack of empirically determined incident and emitted spectra for all the planets), the calculation is essentially wavelength-dependent and thus avoids most of the deficiencies of the heat flow analysis. The same formalism can be applied directly to exact incident and outgoing spectra once these planetary data become available.

The global entropy production of a planet can be determined by considering the change in the frequency ν or wavelength λ distributions of the radiation incident from the Sun, $I_{in}(\nu)$ [J m^{-2}] or $I_{in}(\lambda)$ [J m^{-3} s^{-1}], and that radiated by the planet, $I_{rad}(\nu)$ or $I_{rad}(\lambda)$, including the change in the directional isotropy of the radiation. Planck (1913) determined that the entropy flux $L(\nu)$ [J m^{-2} K^{-1}] due to a given photon energy flux $I(\nu)$ takes the following form (Wu and Liu, 2010):

$$L(\nu) = \frac{n_0 k \nu^2}{c^2} \left[\left(1 + \frac{c^2 I(\nu)}{n_0 h \nu^3}\right) \ln\left(1 + \frac{c^2 I(\nu)}{n_0 h \nu^3}\right) - \left(\frac{c^2 I(\nu)}{n_0 h \nu^3}\right) \ln\left(\frac{c^2 I(\nu)}{n_0 h \nu^3}\right) \right], \quad (1)$$

where n_0 denotes the polarization state, $n_0 = 1$ or 2 for polarized and unpolarized photons respectively, k is the Boltzmann constant, c is the speed of light, and h is Planck's constant. In terms of wavelength ($\lambda = c/\nu$), the corresponding expression is (Wu et al., 2011)

$$
L(\lambda) = \frac{n_0 k c}{\lambda^4} \left[\left(1 + \frac{\lambda^5 I(\lambda)}{n_0 h c^2} \right) \ln \left(1 + \frac{\lambda^5 I(\lambda)}{n_0 h c^2} \right) \right.
$$
$$
\left. - \left(\frac{\lambda^5 I(\lambda)}{n_0 h c^2} \right) \ln \left(\frac{\lambda^5 I(\lambda)}{n_0 h c^2} \right) \right], \tag{2}
$$

which has the units $[\mathrm{J\,m^{-3}\,K^{-1}\,s^{-1}}]$.

The entropy flux (per unit area) at a given surface is thus

$$
J = \int\limits_0^\infty d\lambda \int\limits_\Omega L(\lambda) \cos(\theta)\, d\Omega, \tag{3}
$$

where θ is the angle of the normal of the surface to the incident beam, and Ω is the solid angle subtended by the source at the surface. The total flux crossing the surface is then just this integrated over the entire surface.

Equation (3) with Eq. (2) can be used to compare the entropy production of the planets once the wavelength-dependent energy fluxes, $I_{\mathrm{in}}(\lambda)$ and $I_{\mathrm{rad}}(\lambda)$, have been determined. These data have been obtained by satellite for the Earth (Harder et al., 2005), but have yet to be determined for Earth's neighbors. To allow a comparison of the entropy production of the planets, we therefore make an approximate gray-body approximation for the incident and radiated energy flux. A black-body approximation is valid only if the Sun and planets were in thermodynamic equilibrium, and had an albedo and emissivity equal to 0.0 and 1.0 respectively. The Sun and planets are definitely not in equilibrium (e.g. life on Earth, convection cells on the Sun), so a more accurate gray-body approximation is obtained by taking into account a wavelength-independent albedo α and emissivity ϵ.

The Planck distribution law for the flux of energy emitted normally to the surface, per unit area of the source, per unit solid angle subtended by the source, per unit frequency, for a black-body at temperature T is (Landau and Lifshitz, 1988)

$$
i(\nu) = \frac{n_0 h \nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}, \tag{4}
$$

or, in terms of wavelength (Wu et al., 2011),

$$
i(\lambda) = \frac{n_0 h c^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}. \tag{5}
$$

Therefore, for a planet with emissivity ϵ (gray-body approximation), emitting unpolarized light, the emitted (e) energy flux $I_{\mathrm{rad}}^{\mathrm{e}}$ is

$$
I_{\mathrm{rad}}^{\mathrm{e}}(\lambda) = \frac{\epsilon\, 2 h c^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT_{\mathrm{P}}} - 1}, \tag{6}
$$

where T_{P} is the gray-body equivalent temperature of the planet, obtained from a global energy balance equation and the Stefan-Boltzmann law, including the albedo and emissivity (see, for example, Wu and Liu, 2010).

The planet also reflects a portion, α (albedo), of the Sun's incident energy flux $I_{\mathrm{in}}^{\mathrm{S}}(\lambda)$ into a solid angle of approximately 4π, assuming Lambertian reflection. This dispersion of a directed beam of sunlight also produces entropy. This reflected (r) part of the outgoing radiation is

$$
I_{\mathrm{rad}}^{\mathrm{r}}(\lambda) = \alpha\, I_{\mathrm{in}}^{\mathrm{S}}. \tag{7}
$$

For the energy flux incident from the Sun, knowing that the intensity of the radiation drops as R_{S}^2/d^2, where R_{S} is the Sun's radius and d is the distance of the planet from the Sun, the incident flux at the planet is

$$
I_{\mathrm{in}}^{\mathrm{S}}(\lambda) = \frac{R_{\mathrm{S}}^2}{d^2} \frac{2 h c^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT_{\mathrm{S}}} - 1}, \tag{8}
$$

where $T_{\mathrm{S}} = 5779$ K is the black-body equivalent temperature of the Sun, and $R_{\mathrm{S}} = 6.96 \times 10^8$ m its radius.

The incident entropy flux for the planet in its solar environment can be obtained by assuming that the incident photon beam is parallel. The cross section of this beam captured by the planet is thus πR_{P}^2, where R_{P} is the planet radius, and, therefore, the average incident entropy flux per unit surface area of the planet is just this divided by the planet's surface area $4\pi R_{\mathrm{P}}^2$:

$$
J_{\mathrm{in}}(\lambda) = \frac{1}{4} \int\limits_0^\infty L_{\mathrm{in}}(\lambda)\, d\lambda. \tag{9}
$$

The emitted entropy flux for the planet $[\mathrm{J\,m^{-2}\,K^{-1}\,s^{-1}}]$ is (Eq. 3)

$$
J_{\mathrm{rad}}^{\mathrm{e}}(\lambda) = \int\limits_0^\infty d\lambda \int\limits_\Omega L_{\mathrm{rad}}^{\mathrm{e}}(\lambda) \cos(\theta)\, d\Omega
$$
$$
= \int\limits_0^\infty d\lambda \int\limits_0^{2\pi} \int\limits_0^{\pi/2} L_{\mathrm{rad}}^{\mathrm{e}}(\lambda) \cos(\theta) \sin(\theta)\, d\theta\, d\phi
$$
$$
= \pi \int\limits_0^\infty L_{\mathrm{rad}}^{\mathrm{e}}(\lambda)\, d\lambda. \tag{10}
$$

The reflected entropy flux for the planet can be derived from the albedo times the incident solar energy flux and so has the same geometrical factor as for the incident entropy flux. If we then assume that this radiation is isotropically dispersed into a 4π solid angle (Lambertian reflection), then

$$
J_{\mathrm{rad}}^{\mathrm{r}}(\lambda) = \frac{1}{4} \int\limits_0^\infty d\lambda \int\limits_\Omega L_{\mathrm{rad}}^{\mathrm{r}}(\lambda) \cos(\theta)\, d\Omega = \frac{\pi}{4} \int\limits_0^\infty L_{\mathrm{rad}}^{\mathrm{r}}(\lambda)\, d\lambda. \tag{11}
$$

Table 1. Estimated entropy fluxes of Earth and neighboring planets. See Eq. (12) and text for a definition of the variables. Physical characteristics of the planets were obtained from NASA's Planetary Fact Sheets (NASA, 2011). Effective gray-body equivalent temperatures T_P are obtained by using energy balance equations and the Stefan-Boltzmann law with the assumed wavelength-independent albedo α and emissivity ϵ. Consistency was obtained with NASA's solar irradiances at the top of the atmosphere of the planet, and with the correct partition of the energy according to the bond albedo listed in the table. (The results for all planets have been calculated but are not shown.)

	Venus	Earth	Mars
T_P [K]	197.0	273.0	225.0
Albedo α	0.900	0.306	0.250
Emissivity ϵ	0.756	0.756	0.756
Radius R_P [m]	6.0519×10^6	6.3674×10^6	3.3862×10^6
Distance d [m]	1.0821×10^{11}	1.4960×10^{11}	2.2792×10^{11}
Entropy flux			
J_{in} [W m^{-2} K^{-1}]	0.181	0.099	0.045
J_{rad}^e [W m^{-2} K^{-1}]	0.467	1.243	0.696
J_{rad}^r [W m^{-2} K^{-1}]	0.515	0.103	0.039
J [W m^{-2} K^{-1}]	0.801	1.247	0.689
J_T [W K^{-1}]	3.686×10^{14}	6.352×10^{14}	9.930×10^{13}

The net entropy flux per unit area of the planet is thus

$$J = J_{rad}^e(\lambda) + J_{rad}^r(\lambda) - J_{in}(\lambda)$$

$$= \pi \int_0^\infty L_{rad}^e(\lambda) + \frac{1}{4} L_{rad}^r(\lambda)\, d\lambda - \frac{1}{4} \int_0^\infty L_{in}(\lambda)\, d\lambda. \quad (12)$$

To obtain the total entropy production for the planet, this flux is simply multiplied by the surface area:

$$J_T = J \cdot 4\pi R_P^2. \quad (13)$$

Using Eq. (6) through Eq. (8), together with the physical attributes of the planet given in Table 1, in Eq. (2), and finally integrating over all wavelengths as in Eq. (12) gives the entropy production values for the planets listed in Table 1.

The entropy production of the Earth per unit surface area of $J = 1.247$ W m^{-2} K^{-1} is significantly greater than that of Earth's apparently lifeless neighbors, Venus and Mars. The radiated part of Earth's entropy production per unit surface area is greater than that of Venus and Mars combined. Since Earth is the only planet not following the decreasing entropy production trend per unit area with distance from the Sun, and, of the planets with an atmosphere, the one of greatest entropy production per unit area (data for the other planets not shown), this is suggestive, although not conclusive, of the important role of life in Earth's net entropy production.

If life indeed plays an important role in Earth's entropy production, then this entropy production would occur primarily at Earth's surface where life is predominantly located. Using simple heat flow calculations, Peixoto et al. (1991) (later

Table 2. Estimated values of energy flow Q over temperature differences (T_1, T_2) giving rise to entropy production σ of the major Earth system irreversible processes as determined by Peixoto et al. (1991) and revised by Kleidon and Lorenz (2005). The contribution of each process to the total entropy production is given in the last column.

	Q [W m^{-2}]	T_1, T_2 [K]	σ [mW m^{-2} K^{-1}]	%
Surface dissip.	170	5760, 288	561	63
Atmospheric dissip.	68	5760, 252	258	29
Earth radiated flux	68	288, 252	34	3.8
Latent heat flux	79	288, 266	23	2.6
Frictional heating	19	280, 255	7	0.8
Sensible Heat flux	20.4	288, 280	2.1	0.24

revised by Kleidon and Lorenz, 2005) have estimated the contribution to Earth's entropy production due to the major irreversible processes (Table 2). UV and visible absorption and dissipation in Earth's atmosphere accounts for roughly 29 % of Earth's entropy production, while photon absorption and dissipation at the Earth's surface contributes approximately 63 %. In Sect. 4 to Sect. 6 below, we demonstrate that organic pigments in water play an essential role in this dissipation of sunlight at Earth's surface, which is the first step of the hydrological cycle.

4 Life's thermodynamic function; dissipation and transpiration, not photosynthesis

Life is found almost everywhere on Earth, becoming sparse only where water is scarce. On the Earth's surface, the greatest biomass consists of archaea, prokaryote, and eukaryote life based on photosynthesis. In the sea, photosynthetic phytoplankton (archaea, diatoms, cyanobacteria, and dinoflagellates) can be found in great density at the surface (up to 10^9 organisms/ml), and in the rest of the euphotic zone which extends to a depth of 50 m. Almost all photosynthesis ends at the bottom of the Epipelagic zone at about 200 m. Approaching these depths, special pigments are needed to utilize the only faint blue light that can penetrate the overlying water. On land, diatoms, cyanobacteria, and plants, which evolved from ocean cyanobacteria some 470 million years ago (Wellman and Gray, 2000; Raven and Edwards, 2001), cover almost every available area touched by water and light. Photosynthesizing cyanobacteria have been found thriving in hot-springs at over 70 °C (Whitton and Potts, 2000) and on mountain glaciers and within Antarctic ice (Parker et al., 1982) where absorption of solar radiation and its dissipation into heat by organic and lithogenic material within the ice generates the vital liquid water (Priscu et al., 2005).

The thermodynamic force for driving the process of photosynthesis, which sustains surface life, derives from the low entropy of sunlight and the second law of thermodynamics. In photosynthesis, a high-energy photon in the visible region

of the Sun's spectrum is converted by the chloroplasts into 30 or more low energy photons in the infrared region. A small part of the free energy made available in the process is utilized to extract and fix organic carbon from atmospheric carbon dioxide. In this manner, photosynthetic life is maintained and propagated through the conversion of the low entropy of sunlight into the higher entropy of heat, and thereby contributes to the global entropy production of Earth.

However, that part of the solar spectrum utilized in photosynthesis is small, and thus the entropy-producing potential of photosynthesis is small. Gates (1980) has estimated that the percentage of available free energy (Gibb's, at constant temperature and pressure) in solar radiation that is used in the net primary production of the biosphere is less than 0.1 %. Respiration consumes a similarly small quantity. Of all the irreversible processes performed by living organisms, the process generating by far the greatest amount of entropy on a global scale, the important thermodynamic function of life, is the absorption of and dissipation of sunlight into heat facilitated by organic molecules in water, and thus fomenting evapotranspiration (Hernández Candia, 2007). Great quantities of water are absorbed by the root systems of plants and brought upwards to the leaves and then evaporated into the atmosphere. For example, it has long been known (Brown and Escombe, 1905) that over 90 % of the Gibb's free energy available in the sunlight captured by the leaves of plants is used in transpiration. (Note that free energy dissipation can be associated directly with entropy production only for systems with no net exchange of heat, no enthalpy change.) In the oceans, phytoplankton within the euphotic zone absorb sunlight and transform it into heat that can be efficiently absorbed by the surface water (water absorbs strongly over the infrared but not visible, nor near UV). The temperature of the ocean surface is thereby raised (Kahru et al., 1993) leading to increased evaporation and promotion of the water cycle, hurricanes, and ocean and wind currents.

There appears to be no important physiological need for the vast amount of transpiration carried out by land plants. It is known, for example, that only 3 % of the water drawn up by plants is used in photosynthesis and metabolism. In fact, most plants can grow normally under laboratory conditions of 100 % humidity, at which the vapor pressure in the stoma of the leaves cannot be greater than that of the atmosphere, and therefore transpiration is necessarily zero (Hernández Candia, 2009). Transpiration is often considered as an unfortunate by-product of photosynthesis in which water is unavoidably given off through the stoma of plants, which are open in order to exchange CO_2 and O_2 with the atmosphere (Gates, 1980). Plants consist of up to 90 % water by mass and thus appear to expose themselves to great risk by transpiring so much water.

Another argument is that transpiration is useful to plants since it helps to cool the leaves to a temperature optimal for photosynthesis. This, however, is at odds with the fact that nature has produced numerous examples of efficient photosynthesis at temperatures greater than 70 °C (Whitton and Potts, 2000). In any case, there exist other simpler and less free energy demanding strategies to reduce leaf temperature, such as smaller or less photo-absorbent leaves. On the contrary, the evolutionary record of the history of life on Earth indicates that plants and phytoplankton have evolved new pigments over time to absorb ever more completely the Sun's spectrum. Dense pine forests appear black in the midday sun. Plants appear green not so much for lack of absorption at these wavelengths, as for the fact that the spectral response of the human eye peaks precisely at these wavelengths (Chang, 2000).

Transpiration is, in fact, extremely free energy intensive and, according to Darwinian theory, such a process, with little direct utility to the plant, should have been eliminated or suppressed through natural selection. Plants that are able to take in CO_2 while reducing water loss, by either opening their stoma only at night (CAM photosynthesis) or by reducing photo-respiration (C4 photosynthesis, see below), indeed have evolved 32 and 9 million years ago respectively (Osborne and Freckleton, 2009). However, this water conserving photosynthesis has not displaced the older, heavily transpiring C3 photosynthesis, which is still relevant for 95 % of the biomass of Earth. Rather, new ecological niches in water scarce areas have opened up for the CAM and C4 plants, for example, the cacti of deserts.

Finally, by analyzing latent heat fluxes (evaporation) and the CO_2 flux for plants from various published data sets, Wang et al. (2007) have found vanishing derivatives of transpiration rates with respect to leaf temperature and CO_2 flux, suggesting a maximum transpiration rate for plants, i.e. that the particular partition of latent and sensible heat fluxes is such that it leads to a leaf temperature and leaf water potential giving maximal transpiration rates, and thus also maximal contribution to the hydrological cycle and production of entropy (Wang et al., 2007).

It is here proposed that excessive photon absorption, dissipation, and transpiration have not been eliminated from plants, despite the extraordinary free energy costs and the danger of drying, precisely because the basic thermodynamic function of a plant is to increase the global entropy production of the Earth in its interaction with its solar environment, and this is achieved by dissipating high energy photons into heat in the presence of water, thereby augmenting the global water cycle and wind currents. Analogously, cyanobacteria floating at the surface of oceans and lakes heat the surface water, causing increased evaporation, hurricanes (Gnanadesikan et al., 2010), and ocean currents (see Sect. 6).

5 Biological catalysis of the hydrological cycle

5.1 Life and water

The very existence of liquid water on Earth can be attributed, in large part, to the existence of life (Lovelock, 1988). Physical mechanisms exist that disassociate water into its hydrogen and oxygen components, for example, the photodissociation of water by ultraviolet light (Chang, 2000). Free hydrogen, being very light, can escape Earth's gravity and drift into space, being dragged along by the solar wind. Photo-dissociation of methane has been suggested to be another important route to losing the hydrogen necessary for water (Catlin et al., 2001). This loss of hydrogen would have led to a gradual depletion of the Earth's water, as appears to have occurred on Venus (Lovelock, 2005). By deflecting the solar wind particles, Earth's magnetic field may have helped reduce the effects of the solar wind on hydrogen loss (Hunten, 1993), but life has played an important role in reducing hydrogen loss.

Photosynthetic life releases oxygen from carbon dioxide thereby providing the potentiality for its recombination with the free hydrogen to produce water. For example, hydrogen sulfide is oxidized by aerobic chemoautotrophic bacteria, giving water as a waste product (Lovelock, 1988). Oxygen released by photosynthetic life also forms ozone in the upper atmosphere which protects water vapor and methane in the lower atmosphere from ultraviolet photo-dissociation. In this manner, life on Earth has kept the amount of water on Earth relatively constant since the beginnings of life.

Through mechanisms related to the regulation of atmospheric carbon dioxide and water vapor, first examined in the Gaia hypothesis (Lovelock, 1988), life has also been able to maintain the temperature of Earth within the narrow region required for liquid water (Ventura et al., 2007), even though the total radiation from the Sun has increased by as much as 30 % since the beginnings of life (Newman and Rood, 1977; Gough, 1981).

About 51 % of the free energy arriving from the Sun in short wavelength radiation is absorbed in the biosphere (at the surface of the Earth), the rest being absorbed by the clouds and upper atmosphere (19 %), reflected by the clouds or surface (24 %), or scattered by the atmosphere back into space (6 %) (Pidwirny and Budikova, 2010). About half of the available energy arriving at the Earth's surface is used to evaporate the great quantity of water that is eventually returned to the Earth's surface in the form of rain, hail, or snow (see Table 2). The other half is roughly equally divided between driving ocean and wind currents. A negligible proportion of the free energy absorbed by the biosphere (< 0.2 %) goes into the metabolism and photosynthetic production of biomass.

Earth's water cycle is gigantic. About 496 000 km^3 of water is evaporated yearly, with 425 000 km^3 (86 %) of this coming from the ocean surface and the remaining 71 000 km^3

(14 %) from the land (Hubbart and Pidwirny, 2007). Evaporation rates depend on numerous physical factors such as insolation, photon absorption properties of the atmosphere and water, temperature, relative humidity, and local wind speed. Most of these factors are non-linearly coupled. For example, local variations in sea surface temperature, due to differential photon absorption rates caused by clouds or local phytoplankton blooms, lead to local wind currents. Global winds are driven by latitude variation of the solar irradiance and absorption, and the rotation of the Earth. Relative humidity is a function of temperature, but the condensation of water vapor into clouds is a function of the quantity of microscopic particles available for seeds of condensation, a significant amount of which is derived from living organisms (Lovelock, 1988; Morris et al., 2004; Christner et al., 2008).

The non-linear couplings of the different biotic and abiotic factors affecting the water cycle imply that quantifying the effect of biology on the water cycle is difficult. However, using climate model simulations taking into account most of the important physical factors, Kleidon (2008) has estimated that, without plants, average evaporation rates over land would decrease from their actual average values of 2.4 mm d^{-1} to 1.4 mm d^{-1}, suggesting that plants may be responsible for as much as 42 % of the actual evaporation over land.

5.2 Life and evaporation

Most of the visible and near ultraviolet spectra of sunlight (where the Sun is most intense in terms of free energy) are not readily absorbed by pure water, as can be deduced by the transparency of water at these wavelengths. Only infrared light is efficiently absorbed by water and transferred to the vibrational, and to a lesser extent to the rotational, degrees of freedom of the water molecules. Organic molecules, due to the nature of the strong electronic covalent bonding, are efficient absorbers of sunlight in the visible and ultraviolet regions of the Sun's spectrum. The collective electronic excitations of these molecules have energy levels compatible with the incident photon energies, and these excitations rapidly decay to the ground state through inter-system crossing and vibrational relaxation, particularly if the molecule is in water (Vekshin, 2005). The chlorophyll molecule and associated pigments absorb in the visible region between approximately 400 nm and 700 nm, with chlorophyll *a* peaking in absorption at 410 nm and 680 nm. The nucleic acids, and the proteins containing amino acids with aromatic rings (tryptophan, tyrosine, phenylalanine), are particularly potent absorbers of ultraviolet light within the 200–300 nm region due to the collective electronic excitations of the rings (Chang, 2000). Mycosporine-like amino acids (MAAs) found in phytoplankton absorb across the UVB and UVA regions (310–400 nm) (Whitehead and Hedges, 2002). These absorbed photons, when dissipated into heat, can cause the breaking of hydrogen bonds binding the surrounding water

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molecules, facilitating evaporation at the water surface. Organic molecules can thus be considered as catalysts which allow a greater portion of the Sun's high energy photons to be dissipated through the water cycle.

The intensity of ultraviolet light reaching the Earth's surface today of wavelength less than 290 nm (UVC) is extremely small compared to that of the UVB + UVA + visible light due to absorption by ozone and oxygen, and thus UVC plays a negligible part in the entropy production of the biosphere and associated water cycle. This, however, may not have been the case at the very beginnings of life on Earth (Michaelian, 2009, 2011). During the Archean, the Sun was much more active in the ultraviolet, and the Earth's atmosphere was more reflective and absorptive in the visible and infrared, while much less so in the ultraviolet. This may have been due to (1) the lack of UV absorbing oxygen and ozone; (2) a high layer of sulfuric acid clouds, highly reflective in the visible, as on Venus today, the result of UV photochemical reactions on the common volcanic gases of SO_2, CO_2, and H_2O; (3) clouds of water that preferentially filter infrared over UV (compare Tables 3 and 4 of Sect. 6); and (4) organic haze as on Titan today, the result of UV photochemical reactions on CO_2 and CH_4 (Lowe and Tice, 2004). Life, in particular RNA and DNA, may thus have originated as a catalyst for dissipating photons in the intense UVC region and coupling the resultant heat to the water cycle (Michaelian, 2009, 2011).

Absorption and dissipation into heat of sunlight at the leaves of plants increases their temperature by as much as 20 K over that of the ambient air (Gates, 1980). This leads to an increase of the water vapor pressure inside the cavities of the leaf with respect to that of the colder surrounding air. Water vapor thus diffuses across this gradient of chemical potential from the wet mesophyll cell walls (containing the chloroplasts), through the inter-cellular cavities, and finally through the stoma and into the external atmosphere. There is also a parallel, but less important, circuit for diffusion of H_2O vapor in leaves through the cuticle, providing up to 10 % more transpiration (Gates, 1980). The H_2O chemical potential of the air at the leaf surface itself depends on the ambient relative humidity and temperature, and thus on such factors as the local wind speed and insolation. Diffusion of H_2O vapor into the atmosphere causes a drop in the water potential inside the leaf which provides the force to draw up new water from the root system of the plants.

Evaporation from moist turf (dense cut grass) can reach 80 % of that of a natural water surface such as a lake (Gates, 1980), while that of a tropical forest can often surpass by 200 % of such a water surface. Single trees in the Amazon Rainforest have been measured to evaporate as much as 1180 l day^{-1} (Wullschleger et al., 1998). This is principally due to the much larger surface area for evaporation that a tree offers with all of its leaves as compared to the two-dimensional area projected by the tree onto the surface. Natural water surfaces, in turn, evaporate approximately 8 %

more than distilled water surfaces due to the increased UV and visible photon absorption at the surface as a result of phytoplankton and other suspended organic materials (see Sect. 6.1), including a large component (up to 10^9/ml) of viral and dissolved DNA, resulting from viral lysing of bacteria (Wommack and Colwell, 2000). In surface waters with rich ecosystems, nueston can increase evaporation 3-fold by stirring the skin layer with their flagella (MacIntyre, 1974).

Cyanobacteria have been found to be living within Antarctic ice at depths of up to 2 m. These bacteria and other lithogenic material in the ice absorb solar radiation, which causes the formation of liquid water within the ice even though the outside air temperatures may be well below freezing. This heating from below causes increased ablation and sublimation of the overlying ice at rates as high as 30 cm per year (Priscu et al., 2005), providing another important contribution to the hydrological cycle.

Clouds are an integral part of the water cycle; however, their formation may seem to have a detrimental effect on evaporation since cloud cover on Earth reflects approximately 20 % of light in the visible and ultraviolet regions of the Sun's spectrum (Pidwirny and Budikova, 2010). Clouds absorb the major part of the direct infrared radiation from the Sun, thereby reducing the potential for evaporation at the Earth's surface. However, evapotranspiration is a strong function of the local relative humidity of the air around the leaves of plants or above the surface of the oceans. By producing local cool regions during the day, and local warm regions during the night, clouds are able to maintain the average wind speed at the Earth's surface within dense vegetation at values above the threshold of $0.25\,\mathrm{m\,s^{-1}}$ required to make the boundary-layer resistance to water loss almost negligible in a plant leaf (see for example, Speck; 2003), thereby procuring maximal transpiration rates (Gates, 1980).

Other indications suggesting that a partially clouded Earth may, counter-intuitively, be beneficial to global evaporation are (1) the condensation of water vapor into clouds reduces the absolute amount of water vapor in the atmosphere, meaning reduced humidity at the surface. (2) Clouds bring water to inland regions which allows plants to grow and thus increment land evapotranspiration and thus the size of the water cycle over land. In any case, without clouds, there simply would be no hydrological cycle.

The important question, however, within the context of the hypothesis presented here, is not the evaporation rate, but rather the global entropy production rate under a partly cloudy sky as compared to a clear sky. This is a much more complex issue, because all coupled irreversible processes operating in the ecosphere must be taken into account. As mentioned in Sect. 3, even Lambertian reflection of light produces entropy (on Venus it accounts for half of the total entropy production; see Table 1). Finally, and most importantly, the potential for entropy production is biased towards the visible and UV regions, so the strong absorption of clouds in the infrared, although having an important effect on the

incident energy flow, will have a reduced effect on global entropy production.

5.3 Life and condensation

The water vapor transpired by leaves, or evaporated by phytoplankton, is subjected to general mixing through atmospheric convection and an upward buoyancy caused by water vapor at $0.804\,\mathrm{g\,l^{-1}}$ being less dense than dry air at $1.27\,\mathrm{g\,l^{-1}}$. Water vapor attaining a height corresponding to a temperature of approximately $259\,\mathrm{K}$ ($-14\,°\mathrm{C}$) (Newell et al., 1974) condenses around suspended microscopic particles to form clouds. Over oceans, an important constituent of these microscopic seeds of condensation is the sulfate aerosols produced by the oxidation of dimethyl-sulfide released by phytoplankton (Charlson et al., 1987).

Biological material floating in the atmosphere has been shown to provide the seeds of condensation for rain drops and snowflakes in greater than 95 % of the cases where condensation occurred at temperatures greater than $-10\,°\mathrm{C}$. More than 40 % of this material was determined to be viable bacteria (Morris et al., 2004; Christner et al., 2008). More recently, ice nucleating bacteria have been found in great quantity in the nuclei of hail stones. Christner (2011) has found that ice nucleating strains of *P. syringae* possess a gene that encodes a protein in their outer membrane that binds water molecules in an ordered arrangement. Such regularity on the atomic scale of the surface of these bacteria facilitates condensation of water and the formation of ice at temperatures well above those required for inorganic seeds (Christner, 2011). This ability of bacteria to condense water has been tentatively assigned to an evolved mechanism for promoting their dispersal (Christner et al., 2008). This discovery, however, may be another line of evidence supporting the hypothesis of biological catalysis of the hydrological cycle.

Condensation of the water releases an amount of latent heat of condensation ($2.427 \times 10^6\,\mathrm{J\,kg^{-1}}$) into the upper atmosphere, half of which is then directly radiated into space (oxygen and nitrogen molecules absorb and emit very little at these wavelengths) in an approximate black-body spectrum at about $-14\,°\mathrm{C}$. The Earth maintains its energy balance with space; the total energy incident on the ecosphere in the form of sunlight is equal to the total energy radiated by the ecosphere into space but at red-shifted wavelengths. Energy is conserved while the entropy of the universe is augmented, as required by the first and second laws of thermodynamics respectively.

Makarieva and Gorshkov (2007) have described a biotic pump that operates as a result of a non-equilibrium vertical distribution of water vapor occurring over heavily transpiring woodland areas. Condensation of water vapor above the forest canopy reduces its partial pressure, leading to a region of low pressure above the forest which then sucks in moisture-laden air from neighboring water bodies. Such a pump drives atmospheric moisture from the oceans to much greater distances inland than would otherwise be obtained without forest cover. A prominent example of this is the Amazon River Basin where atmospheric moisture originating at the Atlantic Ocean is transported several thousand kilometers inland rather than the hundreds of kilometers expected without the operation of such a biotic pump. The biotic pump allows vegetation to exist over a much greater area of the Earth's surface, providing, in this manner, an important contribution to the global water cycle and entropy production.

6 The importance of life at the ocean surface skin layer to the hydrological cycle

In contrast to the numerous published works on land transpiration, there appears to be little recognition in the literature of the importance of cyanobacteria and other living and non-living organic matter floating at the ocean surface to evaporation rates. One important exception is Jones et al. (2005) who have determined that phytoplankton can, through increased photon absorption, increase surface temperatures and therefore the outgoing latent heat flux of a lake. Irrespective of other factors such as wind speed and humidity, evaporation rates should at least correlate with the amount of solar radiation absorbed in the sea-surface layer. An indication of the passive effect of biology on photon dissipation and evaporation rates over oceans and lakes can be made by examining the different factors responsible for energy absorption in surface water. Before attempting such an analysis, however, it is first relevant to review the physical and biological nature of the air-sea interface from which evaporation occurs.

The ocean surface skin layer of roughly 1 mm thickness has particular importance to ocean ecosystems since it is the region of mass, energy and momentum transfer with the atmosphere (Hardy, 1982; Soloviev and Lukas, 2006). The upper $50\,\mathrm{\mu m}$ of this layer (the microlayer) hosts an ecosystem of particularly high organic density, up to 10^4 the density of water only slightly below (Hardy, 1982; Grammatika and Zimmerman, 2001). This is due to the scavenging action of rising air bubbles from breaking waves and raindrops, surface tension, and natural buoyancy (Grammatika and Zimmerman, 2001). The organic material consists of cyanobacteria, diatoms, viruses, free-floating RNA/DNA, and other living and non-living organic material such as chlorophyll and other pigments. At depths of between $1\,\mathrm{\mu m}$ and $10\,\mathrm{\mu m}$, the concentration of zooplankton is up to 10 times that of water slightly below (Hardy, 1982).

Most of the heat exchange between the ocean and atmosphere of today occurs from within this upper 1 mm of ocean water. For example, most of the radiated infrared radiation from the sea comes from the upper $100\,\mathrm{\mu m}$ (Schlüssel et al., 1990). About 52 % of the heat transfer from this ocean layer to the atmosphere is in the form of latent heat (evaporation); radiated long-wave radiation accounts for 33 %, and sensible

Table 3. Values of energy deposition per unit time in the sea surface skin layer and the contribution to entropy production for the different wavelength regions assuming clear skies. Energy flux data (1st row) were obtained by graphically integrating the plots given in Gates (1980, Fig. 8.17).

Clear skies	UV (290–400 nm) W m^{-2}	Visible (400–700 nm) W m^{-2}	Infrared (700–10 000 nm) W m^{-2}
Energy flux reaching Earth's surface (total 1029.3 W m^{-2})	50.5 direct 33.7 skylight – 84.2 global (8.2 %)	428.2 direct 53.9 skylight – 482.1 global (46.8 %)	456.3 direct 6.7 skylight – 463.0 global (45 %)
Energy flux absorbed in 1 mm skin layer (pure water)	0.84×10^{-3} ($A_0^{345} = 1.0 \times 10^{-4}$ cm^{-1})	38.6×10^{-3} ($A_0^{550} = 8.0 \times 10^{-4}$ cm^{-1})	9.16 ($A_0^{1050} = 0.2$ cm^{-1})
Energy flux absorbed in 1 mm skin layer (ocean water)	0.84 ($A_{\text{org}}^{345} = 0.1$ cm^{-1})	0.39 ($A_{\text{org}}^{550} = 8.0 \times 10^{-3}$ cm^{-1})	9.16 ($A_{\text{org}}^{1050} = 0.2$ cm^{-1})
% of total entropy production in ocean skin	15.5	7.6	76.9

heat through direct conduction accounts for the remaining 15 %.

During the day, infrared (700–10 000 nm), visible (400–700 nm), and ultraviolet (290–400 nm) light is absorbed at the sea surface. In the NE Atlantic, for example, daytime temperatures at the surface skin layer have been measured to increase on average by 2.5 K (up to 4.0 K under low wind conditions) compared to the practically constant temperature at an ocean depth of 10 m (Schlüssel et al., 1990). Nighttime temperatures at the skin layer, on the contrary, decrease on average by 0.5 K (up to 0.8 K) with respect to the relatively constant temperature at a depth of 10 m. It is thus of interest to determine how much of this daytime heating is due to the organic material in this layer, and to separate the relative contributions due to UV, visible, and infrared absorption. Such a determination, for both clear and cloudy skies, will allow an estimate of the effect of life on photon dissipation and evaporation over oceans and an estimate of the associated entropy production. For the sake of calculation, we take the surface skin layer for light absorption and heat exchange to the atmosphere to be 1 mm (this should be a maximum limit for the relevant thickness for energy exchange since below this depth turbulence and mixing with lower ocean water becomes relevant; Soloviev and Lukas, 2006, and the amount of organic material drops off significantly; Grammatika and Zimmerman, 2001).

Three distinct wavelength regions are considered for the calculation: 290–400 nm (UV) (below 290 nm, almost all light is absorbed by atmospheric O_3 and O_2); 400–700 nm (visible); and 700–10 000 nm (infrared). There is very little energy in sunlight beyond 10 000 nm. The total amount of energy arriving at the sea surface in each wavelength region is first calculated for a clear sky with no clouds and the sun directly overhead. This can be obtained by integrating the area under a plot of the irradiance at the Earth's surface as

a function of wavenumber (e.g. Gates, 1980, Fig. 8.17). The result is given in the first row of Table 3.

To calculate the amount of energy deposited per unit time per unit area in each wavelength region within the 1 mm skin layer of pure water without organic material (salts absorb very little in the visible and UV; Liew, 2002), we use an average water absorption coefficient corresponding to a wavelength at the middle of the UV and visible wavelength regions (345 nm and 550 nm respectively), whereas for the infrared region, we use the absorption coefficient at 1050 nm since this corresponds to the greatest incident contribution not absorbed by water vapor in the atmosphere (Fig. 8.17 of Gates, 1980), and because the irradiance drops off sharply at wavelengths greater than this. Chaplin (2009) gives the following absorption coefficients at these wavelengths for pure water: $A_0^{345} = 1.0 \times 10^{-4}$ cm^{-1}, $A_0^{550} = 8.0 \times 10^{-4}$ cm^{-1}, $A_0^{1050} = 0.2$ cm^{-1}.

The flux of energy deposited in the 1 mm skin layer is then

$$\delta I = I_0 - I(x) = I_0 \left(1 - \exp(-Ax)\right) \tag{14}$$

with $x = 0.1$ cm, and A is the relevant absorption coefficient. The results are given in the second row of Table 3.

To calculate the amount of energy per unit time deposited within the 1mm skin layer of ocean water with organic material for each wavelength region, the absorption coefficients for the ocean surface microlayer at the different wavelengths are needed. Unfortunately, there do not appear to be any published data in this regard. However, Grammatika and Zimmerman (2001) suggest that the skin microlayer contains up to 10^4 times the density of organic material as water slightly below. This factor of 10^4 is an order of magnitude greater than that of the ratio between the densities of organic matter in very turbid coastal waters to that of deep sea water (Wommack and Colwell, 2000). Since attenuation due to particulate scattering (inorganic material absorbs little in the UV

and visible) is at least an order of magnitude less than that due to absorption on dissolved organic material and chlorophyll in turbid coastal waters (Liew, 2002), we can take the absorption coefficients for coastal turbid waters obtained for the Baltic Sea by Bricaud et al. (1981, Fig. 3) as a lower limit surrogate to that of the surface skin layer of the ocean: $A_{org}^{345} = 0.1\,cm^{-1}$, $A_{org}^{550} = 8.0 \times 10^{-3}\,cm^{-1}$, $A_{org}^{1050} = 0.2\,cm^{-1}$. The value for the infrared absorption is the same as that for pure water since organic molecules absorb very little compared to water in this wavelength region. Using Eq. (14) with these values, we obtain the third row of Table 3.

By comparing the third row with the second row of Table 3, it can be stated that on a clear day, with the sun directly overhead (air mass of 1.0), the organic matter floating in the surface skin layer increases the absorption of energy in this layer by about 13 % over what its value would be without this organic matter.

6.1 Increase in surface evaporation due to life in the ocean surface layer

A very rough estimation of the increase in surface evaporation due to the passive effect of organic material in the 1 mm skin surface layer of the ocean can be made assuming that the greatest contribution to the evaporation rate EV is that proportional to the vapor pressure deficit $e_s - e_a$, where e_s is the saturated vapor pressure directly at the water surface, and e_a is the actual vapor pressure of the atmosphere (Gates, 1980),

$$EV \propto e_s - e_a = \beta e_s (1 - RH), \qquad (15)$$

where RH is the relative humidity and β is some constant of proportionality. The saturation vapor pressure increases exponentially with air temperature T (Allen et al., 1998):

$$e_s = 0.6108 \exp\left(\frac{17.27\,T}{T + 237.3}\right) \qquad (16)$$

in units of kPa for T in °C. Differentiation gives

$$\frac{\Delta e_s}{\Delta T} \approx \frac{4098.2 \left[0.6108 \exp\left(\frac{17.27\,T}{T+237.3}\right)\right]}{(T + 237.3)^2}. \qquad (17)$$

Equation (15) gives

$$\Delta EV = \beta \Delta e_s (1 - RH) \qquad (18)$$

assuming that the relative humidity RH is constant with temperature (valid for small temperature changes of the ocean surface and air directly above, other conditions being equal). Therefore, the percentage increase in the evaporation rate is

$$\frac{\Delta EV}{EV} = \frac{\Delta e_s}{e_s} = \frac{4098.2}{(T + 237.3)^2}\,\Delta T. \qquad (19)$$

Since the air immediately above the water surface will rapidly come to thermodynamic equilibrium with the

water skin layer, the change in temperature ΔT of the air above the water surface will be the same as that of the 1 mm water layer. The change in water temperature in the skin layer, with respect to the case without organic material, is proportional to the extra energy deposited ΔE in the surface layer divided by the heat capacity at constant volume of the water, $C_V = 4186.9\,J\,kg^{-1}\,°C^{-1}$, at, say, an ocean temperature of 14.5 °C. The extra energy deposited in the surface skin (due to organic material) can be obtained by integrating the extra energy flux deposited, $0.84–0.084\,(UV) + 0.39–0.039\,(visible) + 9.16–9.16\,(infrared) = 1.11\,W\,m^{-2}$; see Table 3, over the time to, say, midday ($\Delta t = 4\,h \times 60\,min\,h^{-1} \times 60\,s\,min^{-1} = 14\,400\,s$), when the Sun is directly overhead, and over the cosine of the angle of the Sun from the zenith during the morning, giving the total extra energy deposited: $\Delta E \approx 1.11\,J\,s^{-1}\,m^{-2} \times 14\,400\,s \times 0.64 = 10\,175\,J\,m^{-2}$. However, heat will be lost from this layer due to radiation, conduction, and evaporation during the morning. Assuming that half of the extra energy deposited is lost to these processes before midday (i.e. that ocean surface skin layer is a gray-body of effective emissivity 0.5), then at midday the accumulated energy in the surface skin layer would be $0.5 \times 10\,175 = 5088\,J\,m^{-2}$, which corresponds to $5088\,J\,kg^{-1}$ of water for a 1 mm thick layer. The very approximate increase in the ocean skin surface temperature due to organic material is thus

$$\Delta T = \Delta E / C_V = 5088/4186.9 = 1.2\,°C, \qquad (20)$$

which is consistent with the measurements of Jones et al. (2005) who find maximum increases in surface temperatures of approximately 1.5 °C for induced phytoplankton blooms. The percentage increase in evaporation rate is, therefore,

$$\frac{\Delta EV}{EV} = \frac{4098.2}{(14.5 + 237.3)^2} \times 1.2 = 0.077. \qquad (21)$$

Therefore, with the Sun directly overhead on a clear day at the Equator, absorption of UV and visible light on the organic material floating at the ocean surface skin layer increments the evaporation rate of this layer by, very roughly, 8 %.

6.2 Entropy production due to life in the ocean surface layer

The relative contribution of the different wavelength regions to the entropy production in the sea-surface skin layer resulting from photon absorption and dissipation within each wavelength region can now be determined by using Eq. (3) for the absorbed L_{abs} and dissipated L_{diss} entropy fluxes at the ocean surface.

Table 4. Values of energy deposition per unit time in the sea surface skin layer and contribution to the entropy production for the different wavelength regions assuming overcast skies. Energy flux data (1st row) were obtained by graphically integrating the plots given in Gates (1980, Fig. 8.17).

Overcast skies	UV (290–400 nm) W m^{-2}	Visible (400–700 nm) W m^{-2}	Infrared (700–10 000 nm) W m^{-2}
Energy flux reaching Earth's surface (total 341.6 W m^{-2})	22.04 (6.5 %)	274.7 (80.4 %)	44.86 (13.1 %)
Energy flux absorbed in 1 mm skin layer (pure water)	0.22×10^{-3} ($A_0^{345} = 1.0 \times 10^{-4}$ cm^{-1})	0.022 ($A_0^{550} = 8.0 \times 10^{-4}$ cm^{-1})	0.09 ($A_0^{800} = 0.02$ cm^{-1})
Energy flux absorbed in 1 mm skin layer (ocean water)	0.22 ($A_{\text{org}}^{345} = 0.1$ cm^{-1})	0.22 ($A_{\text{org}}^{550} = 8.0 \times 10^{-3}$ cm^{-1})	0.09 ($A_{\text{org}}^{800} = 0.02$ cm^{-1})
% of total entropy production in ocean skin	44.1	43.1	12.8

The total absorbed entropy flux in the ocean surface skin layer with the Sun directly overhead is

$$
J_{\text{abs}} = \int_{\lambda_1}^{\lambda_2} L_{\text{abs}}(\lambda)\,d\lambda
$$

$$
= \int_{\lambda_1}^{\lambda_2} \frac{2kc}{\lambda^4} \left[\left(1 + \frac{\lambda^5 I_{\text{abs}}(\lambda)}{n_0 h c^2}\right) \ln\left(1 + \frac{\lambda^5 I_{\text{abs}}(\lambda)}{n_0 h c^2}\right) \right.
$$
$$
\left. - \left(\frac{\lambda^5 I_{\text{abs}}(\lambda)}{n_0 h c^2}\right) \ln\left(\frac{\lambda^5 I_{\text{abs}}(\lambda)}{n_0 h c^2}\right) \right] d\lambda, \tag{22}
$$

where the absorbed energy flux within each wavelength region between λ_1 and λ_2, per unit wavelength, is

$$
I_{\text{abs}}(\lambda) = \delta E_\lambda / (\lambda_2 - \lambda_1) \tag{23}
$$

where δE_λ is the energy flux deposited in the wavelength region within the ocean surface skin layer (row 3 of Tables 3 and 4). Equation (23) makes the approximation that the energy distribution is flat over the given wavelength region.

The entropy flux of dissipation within the ocean surface skin layer is

$$
J_{\text{diss}} = \pi \int_0^\infty L_{\text{diss}}(\lambda)\,d\lambda
$$

$$
= \pi \int_0^\infty \frac{2kc}{\lambda^4} \left[\left(1 + \frac{\lambda^5 I_{\text{diss}}(\lambda)}{n_0 h c^2}\right) \ln\left(1 + \frac{\lambda^5 I_{\text{diss}}(\lambda)}{n_0 h c^2}\right) \right.
$$
$$
\left. - \left(\frac{\lambda^5 I_{\text{diss}}(\lambda)}{n_0 h c^2}\right) \ln\left(\frac{\lambda^5 I_{\text{diss}}(\lambda)}{n_0 h c^2}\right) \right] d\lambda, \tag{24}
$$

where the dissipated energy flux is that of a black-body normalized by the ratio of the energy flux absorbed in the wavelength region, δE_λ, to the energy flux of a black-body

$E = \sigma T^4$ at a temperature equal to that of the surface skin layer $T = 287.5 + 1.2 = 288.7$ K:

$$
I_{\text{diss}}(\lambda) = \frac{\delta E_\lambda}{\sigma T^4} \frac{2 h c^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}. \tag{25}
$$

The total entropy production per unit area in the ocean surface layer is, finally,

$$
J = J_{\text{diss}} - J_{\text{abs}}. \tag{26}
$$

Dividing the entropy produced in each wavelength region by the sum over all regions gives the percentage contribution to the total for each region (fourth row of Tables 3 and 4). By absorbing and dissipating UV and visible light, the organic matter in the sea surface skin layer contributes about $15.5 + 7.6 = 23.1$ % to the total entropy production due to photon dissipation in this layer on a clear day.

Note that we have treated the surface skin layer independently of the rest of the ocean water, and thus the above calculated relative energy, entropy and evaporation fluxes for the different wavelength regions are therefore those relevant to only the ocean surface skin layer of 1 mm thickness. This is justified on the grounds that (1) there is little convection between the skin layer and deeper ocean water, although there is conduction; (2) the organic density of the skin surface ecosystems (and thus UV and visible absorption properties) is approximately 10^4 greater than deeper ocean water; (3) most infrared radiation from the Sun is absorbed in this layer; and (4) most of the latent heat flux is emitted from this layer. More accurate values for the energy, entropy, and evaporation fluxes within this approximation would require considering this layer superimposed on a thermal heat bath taken to be the rest of the ocean and would require integration to the bottom of the Epipelagic zone (200 m depths) as well as knowledge of thermal convection and conduction as a function of depth in sea water.

Finally, it is interesting to note that the absorption of UV light by organic material in water contributes more than

double the amount of energy deposited in the surface skin layer due to absorption of visible light (Table 3), suggesting that UV light, organic material, and the hydrological cycle may have had a long historical association (Michaelian, 2009, 2011).

Since, because of their electronic characteristics, organic molecules are better dissipaters of short wavelength photons as compared to inorganic material, and because the dissipation of a short wavelength photon contributes more to the entropy production than the dissipation of a long wavelength photon, and if indeed biotic-abiotic evolution is driven by increases in entropy production, then the biotic part of the Earth system should have naturally evolved towards dissipating short wavelength photons. It is thus probably not coincidental that Earth's atmosphere, through the action of living organisms, has evolved to one of relatively low albedo with high transparency, such that the most intense shortest wavelengths of the Sun's spectrum can penetrate the atmosphere and be very efficiently dissipated into heat by organic molecules in contact with liquid water in the biosphere.

In the case of an overcast sky, or high humidity, much less infrared radiation arrives at the ocean surface because of the strong absorption of infrared light by water in the atmosphere (see Fig. 8.17 of Gates, 1980). We take the water absorption coefficients corresponding to the middle of the regions to be again 345 nm for UV and 550 nm for visible, but 800 nm for infrared, since from Fig. 8.17 of Gates (1980) the infrared light distribution transmitted through the atmosphere is shifted notably towards shorter wavelengths due to the preferential absorption of the longer wavelengths by clouds. The results for an overcast day for the sea surface skin layer with and without organic matter are given in Table 4.

Comparing the third row with the second row of Table 4, it can be determined that on an overcast day, with the sun directly overhead (air mass of 1.0), the organic matter floating in the surface skin layer increases the absorption of energy in this layer by about 400 % over what the value would be without the organic matter, with equal contributions coming from UV and visible light. However, the total energy absorbed in this skin layer on an overcast day is only about 5 % that of a clear day, due principally to the comparatively small amount of infrared light that makes it through the clouds. By absorbing and dissipating UV and visible light, the organic matter in this layer contributes a surprising $44.1 + 43.1 = 87.2$ % to the total entropy production on a cloudy day.

Comparing rows two and three of both tables, it is apparent that the organic material at the ocean surface increases the energy deposition from the UV spectral region by 1000 fold, and from the visible region by 10 fold. By absorbing and dissipating UV and visible light on the surface of oceans and lakes, life therefore augments the entropy production of the Earth in its solar environment. Without life at the surface, a greater portion of light would be reflected, increasing the albedo of Earth (Clarke et al., 1970, give measurements for the reduction of water albedo at different frequencies due to

the presence of organic material), and light would penetrate deeper into the ocean, thereby augmenting the overall bulk black-body temperature of the ocean (see, for example, Jones et al., 2005 for the effect of phytoplankton on the temperature profile with depth for a lake). Both effects reduce the entropy production of Earth; greater albedo reduces the amount of available light to dissipate, and penetration of light to greater depth shifts the radiated spectrum (day + night integrated) to shorter wavelengths (see Eq. 5) since this excess bulk heat cannot be as easily coupled to the water cycle as can surface heat.

7 Evidence for evolutionary increases in the hydrological cycle

Plants, far from eliminating transpiration as a wasteful use of free energy, have in fact evolved ever more efficient water transport and transpiration systems (Sperry, 2003). There are general trends to ever increasing transpiration rates over both evolutionary time scales and over shorter ecosystem succession time scales. For example, conifer forests are more efficient at transpiration than deciduous forests principally because of the greater surface area offered by needles for evaporation as compared to leaves. Although both conifers and deciduous trees are now believed to have evolved independently from pteridosperms (Soltis et al., 2002) (in the late Carboniferous), they appear in the late successional stage of ecosystems. Root systems are also much more extensive in late evolutionary and successional species, allowing them access to water at greater depths (Raven and Edwards, 2001).

Pigments distinct from chlorophyll have appeared over the evolutionary history of plants and cyanobacteria, covering an ever greater portion of the intense region of the solar spectrum. Such pigments are known to have little, or no, effect on photosynthesis, for example, the carotenoids in plants, or the mycosporine-like amino acids (MAAs) found in phytoplankton which absorb across the UVB and UVA regions (310–400 nm) (Whitehead and Hedges, 2002). MAAs are small (< 400 Da), water-soluble compounds composed of aminocyclohexenone or aminocycleximine rings with nitrogen or imino alcohol constituents (Carreto et al., 1990) which display strong UV absorption maximum between 310 and 360 nm and high molar extinction (Whitehead and Hedges, 2002). These molecules have been assigned a UV photo-protective role in these organisms, but this appears dubious since, in some cases, more than 20 MAAs have been found in the same organism, each with a different, but overlapping, absorption spectrum, determined by the particular molecular side chains (Whitehead and Hedges, 2002). If their principle function were photo-protective, then their existence in a particular plant or phytoplankton would be confined to those particular UV wavelengths that cause damage to the photosynthetic apparatus, and not to the whole UV broadband spectrum. It is particularly notable that the

total absorption spectrum of red algae, for example, has little correspondence to its photosynthetic activation spectrum (Berkaloff et al., 1971).

There exist complex mechanisms that have evolved in plants to dissipate photons directly into heat, by-passing completely photosynthesis. These mechanisms come in a number of distinct classes and operate by inducing the de-excitation of chlorophyll using dedicated enzymes and proteins. Constitutive mechanisms allow for inter-system crossing of the excited chlorophyll molecule into triplet, long-lived, states which are subsequently quenched by energy transfer to the carotenoids. Inducible mechanisms are mechanisms that can be regulated by the plant itself; for example, changing lumen pH causes the production of special enzymes that permit the non-photochemical de-excitation of chlorophyll. Sustained mechanisms are similar to inducible mechanisms but have been adapted to long-term environmental stress. For example, over-wintering evergreen needles produce little photosynthesis due to the extreme cold but continue transpiring by absorbing photons and degrading these to heat through non-photochemical de-excitation of chlorophyll. Hitherto, these mechanisms were considered as "safety valves" for photosynthesis, protecting the photosynthetic apparatus against light-induced damage (Niyogi, 2000). However, their existence and evolution can now be better understood from a thermodynamic point of view as mechanisms designed to augment the entropy production potential of a plant by increasing photon absorption, dissipation, and transpiration rates.

Plants also perform a free energy intensive process known as photo-respiration in which O_2 instead of CO_2 is captured by the binding enzyme RuBisCO, the main enzyme of the light-independent part of photosynthesis. This capture of O_2 instead of CO_2 (occurring about 25 % of the time) is detrimental to the plant for a number of reasons, including the production of toxins that must be removed (Govindjee et al., 2005), and does not lead to ATP production. There is no apparent utility to the plant in performing photo-respiration and, in fact, it reduces the efficiency of photosynthesis. It has been considered as an "evolutionary relic" (Niyogi, 2000), still existing from the days when O_2 was less prevalent in the atmosphere than today, and CO_2 much more so (0.78 % CO_2 by volume at the rise of land plants during the Ordovician (ca. 470 Ma) compared with only 0.038 % today). However, such an explanation is not in accord with the suggested efficacy of natural selection to eliminate useless or wasteful processes.

Another theory has photo-respiration as a way to dissipate excess photons and electrons and thus protect the plant's photosynthesizing system from excess light-induced damage (Niyogi, 2000). Since photo-respiration is common to all C3 plants, independent of their preferred insolation environments, it is more plausible that photo-respiration, being completely analogous to photosynthesis with respect to the dissipation of light into heat in the presence of water (by

quenching of excited chlorophyll molecules) and subsequent transpiration of water, is retained for its complementary role in photon dissipation and transpiration and thus entropy production.

8 The function of animals

If the primary thermodynamic function of the plants and cyanobacteria is to augment the entropy production of the Earth by absorbing and dissipating light in the presence of liquid water, then it may be inquired as to what is the function of higher mobile animal life. Because of their intricate root system, which allows the plants to draw up water for evaporation from great depths, plants are not mobile and depend on insects and other animals for their supply of nutrients, cross fertilization, and seed dispersal into new environments. Burrowing rodents, for example, facilitate the delivery of bacterial reduced organic nutrients to the surface plants. The mobility and the short life span of many insects and animals with respect to that of plants mean that, through excrement and eventual death, they provide a reliable mechanism for the dispersal of nutrients and seeds.

Zooplankton, crustaceans, and animal marine life in water perform a similar function as insect and animal life on land. These more mobile forms of life distribute nutrients throughout the ocean surface through excrement and death. It is noteworthy that dead fish and sea mammals do not sink rapidly to the bottom of the sea or lake, but remain floating for considerable time on the surface where, as on land, bacteria break down the organism into its molecular components, allowing photon dissipating phytoplankton to reuse the nutrients, particularly nitrogen. It is relevant that many algae blooms produce a neurotoxin with apparently no other end than to kill higher marine life (Flewelling et al., 2005). There is also a continual cycling of nutrients from the depths of the ocean to the surface, as deep diving mammals preying on bottom feeders release nutrients at the surface through excrement and death. Because of this animal-powered nutrient cycling, a much larger area of the ocean surface is rendered suitable for phytoplankton growth, offering a much larger area for efficient surface absorption of sunlight and evaporation of water than would otherwise be the case.

From this thermodynamic view, animal life provides a specialized gardening service to the plants and cyanobacteria, which in turn catalyze the absorption and dissipation of sunlight in the presence of water, promoting the water cycle and entropy production. There is strong empirical evidence suggesting that ecosystem complexity, in terms of species diversity, is correlated with potential evapotranspiration (Gaston, 2000). The traditional ecological pyramid should thus be turned on its pinnacle; instead of plants and phytoplankton being considered as the base that sustains animal life, animals are in fact the unwitting servants of plant and phytoplankton life, obtaining thermodynamic relevance only from

their ability to increase the plant and phytoplankton potential for photon dissipation and evaporation of water.

9   Summary and conclusions

I have argued that the basic thermodynamic function of life (and organic material in general) is to absorb and dissipate high energy photons from the Sun such that the heat can be absorbed by liquid water and eventually be transferred to space in a more degraded form through the water cycle. The coupling of life to abiotic irreversible processes, such as the water cycle, hurricanes, oceans and wind currents, contributes importantly to the global entropy production of Earth. Photosynthesis, although relevant to the spread of cyanobacteria and plant growth, has only minor direct thermodynamic relevance. By catalyzing the water cycle through increased photon absorption, radiation-less photon dissipation, extended root systems, larger surface areas for transpiration, an extensive sea-surface ecosystem, acting as seeds of water condensation, and the ability to spread and colonize most of Earth's surface, life augments the entropy production of the Earth in its interaction with its solar environment. The physical attributes of organic material for performing these functions are what distinguishes it from inorganic material.

I have presented estimates of the effect of ocean surface life on the hydrological cycle and entropy production. Empirical evidence was presented indicating that the evolutionary history of Earth's biosphere is one of increased photon absorption and dissipation over time, whether over shorter successional, or longer evolutionary, time scales.

Finally, I have given arguments for considering a revision of the traditional views of the origin and evolution of life. Instead of a rather tautological individual bottom-up fight for survival against an imposing environment, biology should be seen as a coupled irreversible process operating within a hierarchy of other irreversible processes (including abiotic) in a top-down manner to augment the global entropy production of Earth. Increases in the global entropy production of Earth are the driving forces behind the origin and evolution of life.

The thermodynamic perspective presented here ties biotic processes to abiotic processes, co-evolving towards the universal goal of increasing Earth's global entropy production. Although this view is completely consistent with, and has been inspired by, the wisdom of Gaia (Lovelock, 1988, 2005), there is a distinction; the hypothesis of Gaia suggests that mixed biotic-abiotic control mechanisms have evolved to maintain the conditions on Earth suitable to life, i.e. in the interest of life. It is here suggested instead that these biotic-abiotic mechanisms have evolved to augment the entropy production of Earth in its solar environment, principally, but not exclusively, through the facilitation of the water cycle. Life, as we know it, is an important, perhaps even inevitable, but probably not indispensable, catalyst for the production of entropy on Earth.

Important aspects that remain to be considered within this thermodynamic framework are (1) the oscillation of the Earth between different climate regimes (e.g. glaciations) in relation to entropy production, (2) implications of the proposed function of life to the existence of life throughout the universe, and (3) the importance of considering the thermodynamic function of life in investigations concerning the origin and evolution of life on Earth (Michaelian, 2009, 2011).

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